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A novel structure for removal of pollutants from wastewater

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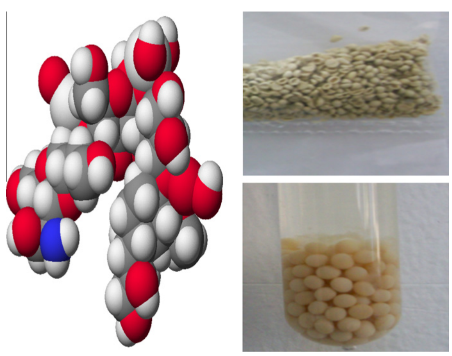
HIGHLIGHTS

- Quantum mechanical model for aquatic plant.
- A microsphere from natural resources.
- Removal and recovery of Pb(II).

GRAPHICAL ABSTRACT



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ABSTRACT

Dried water hyacinth was subjected to molecular modifications using quantum mechanical calculations. The model simulates the modified plant as 3 cellulose units, one lignin and some metal oxides namely CaO; FeO and $Al(OH)_3$ are attached through O-Linkage. The model suggests the ability to remove inorganic pollutants from wastewater according to unique hydrogen bonding and high total dipole moment. Based on this model microspheres are synthesized in the laboratory from dried water hyacinth and chitosan following self-assembly method. FTIR spectrum of microspheres exhibits only the characteristic bands for raw materials which give strong evidence that the formed material is a composite. The analysis of SEM micrographes of microspheres showed that the fibers of water hyacinth are imbedded in the crosslinked chitosan matrix. Batch adsorption kinetic models revealed that the sorption of lead ions on microsphere was very fast and the equilibrium was rapidly attained within 30 min. and properly correlated with the second-order kinetic model. Different models of isotherm sorption were used to describe the Pb (II) adsorption onto microspheres. From Langmuir isotherm, the maximum adsorption capacity (q_{max}) for Pb(II) was 312.5 mg/g, which is about 3 times higher than that of the crude hyacinth. The free energy (E) was 15.798 kJ/mol which shows that the sorption process is endothermic and the mechanism of reaction is an ion-exchange. Even after four cycles of adsorption–desorption, the adsorption capacity was maintained and the decline in efficiency was less than 10%.

Introduction

Pb(II) is being intensively released into the environment as a result of several industrial activities, such as metal plating, microelectronics, battery manufacture, tanneries, oil refining, and mining. It spreads into the environment through soils and water streams and accumulates along the food chain, resulting in a high risk to human health [1,2]. As it does not degrade biologically, the control of Pb(II) pollution has special importance for both organisms that live in water and those that benefit from water [3]. Hence, the development of efficient techniques for the removal

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of Pb(II) ions from wastewaters is an important task in terms of protection of public health and environment. A number of technologies such as adsorption, chemical oxidation, precipitation, solvent extraction, ion exchange, membrane processes, and reverse osmosis have been developed for the removal of metal ions from aqueous solutions [4]. Among them, the adsorption technique is found to be the most effective treatment process with selection of a proper adsorbent [4,5]. Application of new trends in water treatment is an environmental challenge. Chitosan is easily prepared from chitin, the most abundant in nature after cellulose [6]. Chemical modification of chitosan produces materials with a variety of physical and mechanical properties [7–9]. For example, chitosan films and fibers can be formed utilizing cross-linkers and adapted techniques for altering from other polysaccharides, such as treatment of amylose with epichlorohydrin [10]. Like hyaluronic acid, chitosan is not antigenic and is a well-tolerated implanted material [11]. Chitosan can easily be prepared in many forms, including, films and membranes. The basic technique for the casting of chitosan films and fibers was early developed [12,13]. Water hyacinth has received attention because of its ability to remove pollutants from aquatic systems [14]. While it reduces sunlight penetration and lowers oxygen content in water, which has a great impact on water ecosystem [15,16]. Water hyacinth could be used in its dry form after modification to remove Cd from polluted water [17]. Furthermore the plant was successfully used to remove both organic and inorganic pollution from water [18].

Based upon the above considerations, the molecular structure of water hyacinth is simulated using semiempirical PM5. Furthermore microspheres were prepared from dried water hyacinth and chitosan, and then examined by FTIR. The ability of this novel structure for removal and for recovery of lead is tested.

Materials and methods

Calculation details

All calculations were performed on personal computer using Cigress program system at Spectroscopy Department, National Research Centre [19]. Geometries of the studied structures were optimized at semiempirical PM5 [20,21] method and vibrational spectra were calculated at the same level of theory. The frontier molecular orbitals (highest occupied molecular orbital, HOMO and lowest unoccupied molecular orbital, LUMO) were calculated at the same level of theory.

Reagents and sampling

Chitosan low molecular weight was purchased from ABCO Laboratories (Eng. Ltd., Gillingham, England).

$Pb(NO_3)_2$ is the salt used in the preparation of stock standard solution (1000 mg/L) of analytical grade from Merck (Darmstadt, Germany). The synthetic solutions were then prepared by diluting the stock standard.

Sodium tripolyphosphate (TPP) $Na_5O_{10}P_3$, molecular weight 367.86 was purchase from Mallinckrodt. Inc. (Paris, France).

Area of plant collections

Triplicates of water hyacinth were collected from River Nile at Rod El-Farag, Cairo. Samples were washed with deionized water and then divided into root and shoot. Dried separately at 105 °C for 24 h. The dried plants (root and shoot) were ground in a bladed mixer to less than 0.2 mm.

Preparation of microspheres

About 1 g chitosan is dissolved in 30 mL dilute acetic acid (2% (v/v)), a suspension of water hyacinth dry matter was dropped into the chitosan solution with steering for 1 h and the mixture was treated with ultrasonic path for 30 min.

The solution was dropped through a Peristaltic Pump into a gently shaken 100 mL of Sodium tripolyphosphate (TPP) solution at pH 8.6.

The chitosan solution was dropped into the TPP solution and the gelled spheres are formed instantaneously. The solidified spheres were filtered; rinsed; air dried and kept in a dry container for further use.

Batch sorption experiments

In order to explore the effect of contact time, quantity of adsorbent, and the initial concentration of adsorbate, a series of batch experiments were conducted. Batch adsorption was performed by agitating specified amount of adsorbent in 100 mL of metal solution of desired concentration at constant temp. 25 ± 0.2 °C and pH 5.0 ± 0.1 in 125 mL stoppered bottles. The samples were filtered (using Whatman No. 42 filter paper) and analyzed for the concentration of Pb(II) ions remaining in the solution.

Calculation of cation uptake by microspheres

All the experiments were carried out in triplicate. The percent relative standard deviation of the measurements was calculated and considered acceptable if the value was lower than 5%; otherwise, the data were discarded. The percentage of Pb(II) removal by the microspheres during the series of batch investigations was determined using the following equation:

$$\text{Removal}\ (\%) = [(C_0 - C_f)/C_0] \times 100 \quad (1)$$

where C_0 and C_f are the initial and equilibrium concentration (mg/L) of Pb ions in solution, respectively.

Sorption kinetics of microspheres for Pb(II) uptake

The kinetic studies were carried out by shaking 2 g/L of the dried microsphere in 100 mL of Pb(II) ions with an initial concentration of 50 mg/L at different time periods (5, 10, 20, 30, 60, 90, 120 min). The pH of the synthetic solution was 5.0 ± 0.1. Various models were evaluated to describe sorption kinetics. The most commonly used models are pseudo first-order, pseudo-second-order and Elovich kinetic model.

Effect of microsphere dosage

The *microsphere* dosage was varied from 0.25–3.0 g/L using a fixed volume of 100 mL of Pb(II) with an initial concentration 50 mg/L at the equilibration time for lead removal and at constant temp. 25 ± 0.2 °C and pH 5.0 ± 0.1.

Sorption isotherms

The sorption isotherms were measured by varying the initial Pb (II) ions concentration from 100 to 400 mg/L and the other optimum operating conditions for the highest removal efficiency of microspheres are kept constant. Different sorption models described by Volesky [22] were used for comparison with experimental data.

Desorption and reusability studies

The recovery and reusability of microspheres is an important parameter related to the potential application of adsorption technology. In this study, microspheres bound to Pb (II) were transferred to a flask containing 100 mL of brine solution (0.5 g NaOH and 5% NaCl) as a desorbing agent to determine desorption